

# Acid recycling to optimize citric acid-modified soybean hull production

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## Abstract

Modification of soybean hulls with citric acid (CA) improves the metal ion binding capacity of the hulls. A process for this modification has been developed. However, the process must be optimized for it to be cost effective. In this regard, the objectives of this study were (1) to develop a wash procedure to remove non-reacted or residual CA after soybean hull modification in order to maximize the amount of non-reacted acid removed, but minimize the subsequent effect on the product's ability to adsorb copper ion ( $\text{Cu}^{2+}$ ), and (2) to determine whether recycling non-reacted acid in the modification process, along with unused acid, can produce a product with similar copper ion adsorption compared with the use of unused acid only. To meet these objectives, an effective water washing procedure was developed to remove the residual CA associated with the modified soybean hulls. This washing procedure included removal of non-reacted acid, evaporation of excess water to the original volume of acid solution used, and addition of unused CA to reconstitute the solution to its original molarity. Reconstituted CA solutions prepared in this manner were used through three cycles of soybean hull modification. The effectiveness of the reconstituted CA to modify soybean hulls after each cycle was measured by the modified hulls ability to bind copper ions in solution. After three reaction cycles, there was a 7% reduction in copper ion adsorption. In general, two water wash cycles were necessary to remove sufficient non-reacted CA so that metal ion binding of the hulls was not affected, and the use of residual CA to modify soybean hulls can be successfully accomplished with only a small reduction in copper ion binding.

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## 1. Introduction

Soybean hulls are a by-product of soybean processing and occur in great abundance on an

annual basis. In crop year 2001, 6.3 billion kg of hulls were produced in the US ([Agricultural Statistics, 2002](#)). Most of the hulls are used in animal feed as a low value additive. This under-utilized by-product could be converted to products of greater value, such as adsorbents, that can be used for the removal of metal ions from water and wastewater streams. Several published studies have shown the utility of soybean hull modification for

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the enhancement of their metal ion-adsorbing properties (Laszlo, 1987; Laszlo and Dintzis, 1994; Marshall and Champagne, 1995; Marshall and Johns, 1996; Marshall et al., 1999).

A process has been developed to substantially enhance the metal ion binding properties of soybean hulls by modification with citric acid (CA) (Marshall et al., 1999). This process has been examined in terms of the characteristics of the final product, such as metal ion binding and attrition, and comparisons were made to commercial cation exchange resins (Marshall et al., 2000, 2001a) and in terms of the modification process, such as modification of agricultural by-products other than soybean hulls (Wartelle and Marshall, 2000) and a process description with concomitant product cost (Marshall et al., 2001b).

In an attempt to scale-up the modification process based on our laboratory findings, we recognized that the recovery and reuse of non-reacted CA was of paramount importance because CA was determined to be the most costly component in the process and its use had to be conserved (Marshall et al., 2001b). While general scale-up conditions were defined by Marshall et al. (2001b), the conditions necessary for removal of non-reacted CA and data on the modification of soybean hulls with recycled acid were not determined.

The objectives of this study were to develop a wash procedure to maximize the removal of non-reacted CA from modified soybean hulls to develop a product with maximum metal ion adsorption, and to determine whether non-reacted acid could be combined with unused acid and reused to modify hulls without a decrease in metal ion adsorption.

## 2. Materials and methods

### 2.1. Materials

Soybean hulls were supplied by Owensboro Grain Company (Owensboro, KY). Reagent grade CA was purchased from Sigma Chemical Company (St. Louis, MO). Other chemicals were also purchased as reagent grade.

### 2.2. Methods

Soybean hulls were sieved to retain the 10–20 mesh (2.00–0.85 mm) fraction and used without further treatment.

#### 2.2.1. Preparation of CA-modified soybean hulls

Approximately 100 g samples of soybean hulls were reacted with 0.6 M CA in 190 mm × 100 mm crystallization dishes. The modification procedure of Marshall et al. (2001b) was used, where the hull-acid slurry was reacted for 1.5 h at 120 °C, then washed by an ‘agitation’ procedure, where the agitation procedure used various conditions of water temperature and different water:hull ratios as described later. The washed, modified hulls were dried at 60 °C for 16 h and used for analysis of Cu<sup>2+</sup> uptake. The moisture content of the dried hulls was normally 5–8%.

#### 2.2.2. Removal of non-reacted CA

Modified hulls (100 g) were transferred to 4 l beakers containing either 2 l of water, for a hull:water ratio of 1:20 or 4 l of water, for a hull:water ratio of 1:40. Samples at both hull:water ratios were heated to either 40 or 60 °C on a hotplate. Because ambient temperature was about 25 °C, samples designated 25 °C were washed at room temperature. The samples were stirred with an overhead stirrer for 15 min, maintaining the specified temperature. The slurries were vacuum filtered in a Büchner funnel (Whatman #4 filter paper) and the wash water was saved. The wet hulls were then transferred back to the beakers for additional wash cycles at the specific water:hull ratio and wash temperature until a total of five wash cycles were completed. A 2 g sample of hulls was taken after each wash cycle and dried at 60 °C for evaluation of copper ion adsorption. The washes from each cycle were saved as separate samples and kept at 80 °C until all water had evaporated. The residues in the beakers were then weighed. The hull samples were dried at 60 °C to a moisture content of 5–8%.

### 2.2.3. Reuse of non-reacted CA for reaction with unwashed soybean hulls

For experiments involving reuse of non-reacted CA, 7.5 g of unwashed soybean hulls were treated with 50 ml of 0.6 M CA and allowed to imbibe the solution for 30 min. The hulls were dried at 60 °C for 2 h. The hulls were then reacted at 120 °C for 1.5 h. At this point, the modified hulls were water washed employing the agitation method at 25 °C using a hull:water ratio of 1:40. These conditions were repeated a total of four times. The residues from each of the five water washes were evaporated at 80 °C to dryness. The residue contained approximately 80% CA that had not reacted with the hulls. The weight of the residue was recorded and crystalline CA was added to the residue and diluted to 50 ml to reconstitute the solution to 0.6 M. This solution, which contained both reclaimed and unused CA, was used in a reaction with a fresh sample of hulls. This process was repeated a total of three times. After treatment with either the original CA solution or with solutions containing both unused and reclaimed acid, the modified hulls were dried at 60 °C to a moisture content of 5–8% and taken for  $\text{Cu}^{2+}$  adsorption.

### 2.2.4. Copper ion adsorption

The copper ion adsorption procedure described by Marshall et al. (1999) was used in this study. A Leeman Labs Profile dual-view Inductively Coupled Plasma spectrometer (Leeman Labs, Inc., Hudson, NH) was used to analyze copper remaining in solution at 324.754 nm in axial mode. The amount of copper adsorbed per gram of hulls was determined on a dry weight basis.

### 2.2.5. Statistical analysis

Data were analyzed (duplicate determinations) by an analysis of variance using Tukey's multiple comparison test (Sokal and Rohlf, 1995) to compare mean copper ion adsorption values of CA-modified hulls exposed to different wash treatments and reuse conditions. Dunnett's procedure (Walpole and Myers, 1989) for comparing treatments to a control was used to compare the effect of recycling CA to a sample modified with no reused acid. Significant differences in mean values were maintained at  $\alpha = 0.05$ .

## 3. Results and discussion

### 3.1. Removal of excess CA

Our original modified hull wash procedure (Marshall et al., 1999) used about 200 ml of wash water per gram of modified hulls and normally only 3 g of hulls were washed. The hulls were given four or five separate wash treatments and the absence of citrate ion was tested in the final wash by treating it with lead nitrate solution. However, this method gave no indication of the minimum amount of wash water required to remove excess acid. Information on the minimum amount of water to effectively remove non-reacted CA would help conserve water upon process scale-up and reduce the amount and cost of energy required to concentrate the CA-containing wash water in an evaporator.

Both the amount and percentage of CA recovered at two different hull:water ratios and three different wash temperatures using the agitation wash method are given in Table 1. The first wash appeared to be the most critical for removal of excess CA. Between 84 and 92% of the total acid extracted after five wash cycles could be recovered from the first wash. Removal of CA after two washes ranged from 93 to 97% of the total acid extracted. After three washes, the percent CA recovered increased from 95 to 99% of the total acid extracted after five wash cycles. The influence of both the hull:water ratio and wash temperature on the recoveries after any of the wash steps appeared to be small. Recoveries ranged from 51.7 to 59.6% of the total amount of original CA added to the hulls, and did not seem to be dependent upon temperature or ratio of hulls to wash water.

Ideally, all of the non-reacted CA should be removed from the modified hulls in order to maximize acid recovery and minimize the cost of CA in the modification process, especially if the acid can be reused or recycled. However, to achieve this result, repeated washing of the hulls, perhaps as many as five wash cycles, may be necessary and would be very time consuming from a process perspective. From a practical standpoint, such as occurring in a manufacturing

Table 1

Total amount of excess CA recovered and percent CA recovered after five wash cycles at two hull:water ratios and three different wash temperatures using the agitation wash method

Wash cycle	CA recovered (g) at 25 °C		CA recovered (g) at 40 °C		CA recovered (g) at 60 °C	
<i>Hull:water ratio</i>	1:20	1:40	1:20	1:40	1:20	1:40
1	40.2 (92) <sup>a</sup>	41.6 (91)	37.7 (84)	41.0 (90)	35.3 (89)	40.1 (89)
2	1.6 (95)	2.4 (96)	6.0 (97)	2.7 (96)	2.7 (96)	2.0 (93)
3	1.3 (98)	0.9 (98)	0.8 (99)	0.9 (98)	0.9 (98)	1.0 (95)
4	0.4 (99)	0.3 (99)	0.1 (99)	0.6 (99)	0.6 (99)	1.4 (98)
5	0.3 (100)	0.6 (100)	0.5 (100)	0.2 (100)	0.2 (100)	0.7 (100)
<i>Total recovered (g)</i>	43.8	45.8	45.1	45.4	39.7	45.2
<i>Recovery (%)</i>	57.0	59.6	58.7	59.1	51.7	58.8

Values in the table represent a single experiment at each wash temperature and hull:water ratio.

<sup>a</sup> Values in parentheses represent the percent of CA recovered at each wash cycle based on a cumulative value and compared to the total CA recovered.

facility, only one washing would be the best path to follow. Under these conditions, throughput time would be minimal and maximum process throughput could be achieved.

### 3.2. Effect of non-reacted CA removal on copper ion adsorption

In order to decide how many hull washes were sufficient using the agitation wash method, one should monitor changes in metal ion adsorption with each wash cycle and determine whether changes occur in the ability of the different samples to bind the metal ion. The effect of wash cycle on copper ion adsorption is presented in Table 2. With the exception of one hull:water ratio (1:20 at 60 °C), a significantly greater amount of

copper ion was removed using modified hulls exposed to two wash cycles than to modified hulls exposed to only one wash cycle. Under four of the six experimental conditions, copper ion adsorption was not improved by subjecting the modified hulls to more than two wash cycles. Only under conditions of a 25 °C wash at a hull:water ratio of 1:20 and a 60 °C wash at a hull:water ratio of 1:40 were more than two wash cycles required to optimize copper ion adsorption. With two wash cycles, 93–97% of the excess CA had been removed (Table 1). Also, after two wash cycles, the variability of copper ion adsorption is such that there appears to be little difference among modified hulls washed at different wash temperatures and between modified hulls washed at two distinct hull:water ratios except for the two conditions noted above. Given

Table 2

Copper ion adsorption of CA-modified soybean hulls washed at three different temperatures and two different water:hull ratios using the agitation wash method

Wash cycle	25 °C Wash		40 °C Wash		60 °C Wash	
<i>Hull:water ratio</i>	1:20	1:40	1:20	1:40	1:20	1:40
1	1.57±0.00 e	1.70±0.03 d	1.78±0.01 b	1.78±0.01 d	1.74±0.02 a	1.57±0.01 e
2	1.77±0.01 c	1.82±0.01 b	1.85±0.01 a	1.88±0.00 b	1.89±0.03 a	1.67±0.02 d
3	1.80±0.00 b	1.77±0.03 c	1.78±0.02 d	1.88±0.01 b	1.85±0.01 a	1.87±0.06 c
4	1.90±0.01 a	1.76±0.02 c	1.78±0.00 c	1.88±0.01 c	1.82±0.00 a	1.88±0.01 b
5	1.77±0.03 d	1.84±0.00 a	1.84±0.00 a	1.89±0.01 a	1.89±0.04 a	1.90±0.01 a

Mean ± S.E.M. of duplicate determinations. Adsorption values given as millimoles of Cu<sup>2+</sup> adsorbed/g dry weight of modified hulls. Tukey's multiple comparison test was used to compare means within a treatment with  $\alpha = 0.05$ . Samples with the same letters are not significantly different from each other.

the higher costs incurred to the manufacturer by heating wash water above 25 °C, the 25 °C wash at a hull:water ratio of 1:40 is a more practical choice for the conditions that require only two wash cycles.

One must keep in mind that non-reacted CA remaining on the hulls will reduce metal ion adsorption. In batch assays, as conducted for Table 2, non-reacted CA will leach from the modified hulls and sequester or chelate metal ions in solution. The sequestered metal ions would be unavailable for binding with the CA attached to the hulls. Therefore, the solution presented for analysis would contain both chelated and non-chelated metal ions and the metal ion concentration in solution would be greater than a solution with only non-chelated metal ion.

Based on the results presented in Table 2, removal of 93–97% of the excess CA should result in a product with good copper ion binding characteristics without resorting to more than two wash treatments.

### 3.3. Copper ion adsorption using recycled CA

Solutions of 0.6 M CA containing unused acid and both recycled and unused acid were used to modify unwashed soybean hulls. After modification, the hulls were evaluated for copper ion adsorption and the results presented in Table 3. The results indicate that the sample modified with only unused CA had the highest copper ion

adsorption. Successive use of recycled CA, in combination with unused acid, resulted in lower copper ion binding values until a third recycle was attempted. An increase was seen in adsorption after the second cycle of using both reused and unused acid. We have no explanation for this result at this time. Overall, only a 10% reduction in copper ion adsorption was observed between the highest and lowest adsorption values. Copper ion adsorption differences between the initial treatment and the third recycle was shown to be insignificant. An average recovery of 53% was observed.

## 4. Conclusions

A wash method, designated the ‘agitation wash method’ was defined for removing non-reacted CA from soybean hulls after modification. Process variables, such as hull:water ratio, wash water temperature and number of washes were optimized for the effective removal of non-reacted CA. The process resulted in a high quality product with optimal activity towards metal ions. The wash procedure is important for future scale-up to help determine quantities of water required, to calculate wash tank and evaporator size and cost, and to estimate throughput time.

A study on the optimization and estimated production cost of CA-modified soybean hulls (Marshall et al., 2001b) assumed that non-reacted CA could be reused and combined with unused acid to modify additional batches of hulls with little, if any, loss of metal ion binding in the final product. However, no data was shown to back up this assumption. The present study indicates that, at least for a limited number of exposures (three) to both unused and reused acid, this assumption is valid. This information also has future scale-up considerations. We determined that about 55% of the original CA was non-reactive and could be removed by water washing. Because this acid can be reused, significant cost savings can be achieved by recycling acid rather than using unused acid for each batch of soybean hulls.

Table 3  
Effect of recycling CA on copper ion adsorption of CA-modified soybean hulls

Treatment	Copper ion adsorption (mmol/g hulls)
Initial (unused acid only)	1.75 ± 0.01 a
First recycle	1.68 ± 0.01 a
Second recycle	1.57 ± 0.02 b
Third recycle	1.63 ± 0.01 a

Mean ± S.E.M. of duplicate determinations. Values determined on a dry weight basis. Dunnett’s procedure was used to determine significance between the three recycle samples and initial (control) sample at  $\alpha = 0.05$ . Treatments with the same letters are not significantly different from the control.

## 5. Disclaimer

Mention of names of companies or commercial products is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the US Department of Agriculture over others not mentioned.

## References

- Agricultural Statistics 2002. USDA, National Agricultural Statistics Service, US Government Printing Office, Washington, DC.
- Laszlo, J.A., 1987. Mineral binding properties of soy hull. Modeling mineral interactions with an insoluble dietary fiber source. *J. Agric. Food Chem.* 35, 593–600.
- Laszlo, J.A., Dintzis, F.R., 1994. Crop residues as ion-exchange materials. Treatment of soybean hulls and sugar beet fiber (pulp) with epichlorohydrin to improve cation-exchange capacity and physical stability. *J. Appl. Polym. Sci.* 52, 531–538.
- Marshall, W.E., Champagne, E.T., 1995. Agricultural by-products as adsorbents for metal ions in laboratory prepared solutions and in manufacturing wastewater. *J. Environ. Sci. Health A* 30, 241–261.
- Marshall, W.E., Johns, M.M., 1996. Agricultural by-products as metal adsorbents: sorption properties and resistance to mechanical abrasion. *J. Chem. Technol. Biotechnol.* 66, 192–198.
- Marshall, W.E., Wartelle, L.H., Boler, D.E., Johns, M.M., Toles, C.A., 1999. Enhanced metal adsorption by soybean hulls modified with citric acid. *Bioresource Technol.* 69, 263–268.
- Marshall, W.E., Wartelle, L.H., Boler, D.E., Toles, C.A., 2000. Metal ion adsorption by soybean hulls modified with citric acid: a comparative study. *Environ. Technol.* 21, 601–607.
- Marshall, W.E., Wartelle, L.H., Chatters, A.Z., 2001a. Comparison of attrition in citric acid modified soybean hulls and commercial cation exchange resins. *Ind. Crop. Prod.* 13, 163–169.
- Marshall, W.E., Chatters, A.Z., Wartelle, L.H., McAloon, A., 2001b. Optimization and estimated production cost of a citric acid-modified soybean hull ion exchanger. *Ind. Crop. Prod.* 14, 191–199.
- Sokal, R.R., Rohlf, F.J., 1995. *Biometry—The Principles and Practice of Statistics in Biological Research*, third ed., W.H. Freeman, New York, pp. 240–252.
- Walpole, R.E., Myers, R.H., 1989. *Probability and Statistics for Engineers and Scientists*, fourth ed., Macmillan, New York, pp. 463–534.
- Wartelle, L.H., Marshall, W.E., 2000. Citric acid modified agricultural by-products as copper ion adsorbents. *Adv. Environ. Res.* 4, 1–7.